

LAUNDRY AND CLEANING COMPOSITIONS

Field of the invention

The present invention relates to laundry and cleaning compositions comprising a product of reaction between an amino functional polymer comprising at least one primary and/or secondary and/or secondary amine group, and a perfume component, in particular aldehyde or ketone perfumes.

Background of the invention

Laundry and cleaning products are well-known in the art. However, consumer acceptance of laundry and cleaning products is determined not only by the performance achieved with these products but also by the aesthetics associated therewith. The perfume components are therefore an important aspect of the successful formulation of such commercial products.

It is also desired by consumers for laundered fabrics to maintain the pleasing fragrance over time. Indeed, perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carried-over from an aqueous laundry bath onto fabrics is often marginal and does not last long on the fabric. Furthermore, fragrance materials are often very costly and their inefficient use in laundry and cleaning compositions and ineffective delivery to fabrics results in a very high cost to both consumers and laundry and cleaning manufacturers. Industry, therefore, continues to seek with urgency for more efficient and effective fragrance delivery in laundry and cleaning products, especially for improvement in the provision of long-lasting fragrance to the fabrics.

One solution is to use carrier mechanisms for perfume delivery, such as by encapsulation. This is taught in the prior art and described in U.S. 5,188,753. ✓

Still another solution is to formulate compounds which provide a delayed release of the perfume over a longer period of time than by the use of the perfume itself. Disclosure of such compounds may be found in WO 95/04809, WO 95/08976 ✓ and co-pending application EP 95303762.9 ✓

However, notwithstanding the advances in the art, there is still a need for a compound which provides a delayed release of the perfume component.

That need is even more acute for perfume ingredients which are characteristic of the fresh notes, namely the aldehydes and ketones perfume ingredients. Indeed, whilst these provide a fresh fragrance, these perfumes are also very volatile and have a low substantivity on the surface to be treated like fabrics.

Accordingly, it is a further object of the invention to provide a laundry and cleaning composition comprising a perfume component which provides a fresh fragrance and is substantive to the treated surface.

The Applicant has now found that specific reaction products of an amino functional polymer comprising at least one primary and/or secondary amine group with an active aldehyde or ketone, such as imines compounds, also provide a delayed release of the active such as a perfume.

Imine compounds are known in the art under the name of Schiff bases which is the condensation of an aldehyde perfume ingredient with an anthranilate. A typical description can be found in US 4853369. ✓ By means of this compound, the aldehyde perfume is made substantive to the fabrics. However, a problem encountered with these schiff bases is that the methylantranilate compound also exhibits a strong scent, which as a result produces a mixture of fragrances, thereby reducing or even inhibiting the aldehyde and/or ketone fragrance perception.

To achieve such perfume composition with comparabl aldehyde or ketones fresh notes whilst still having satisfactory fabric substantivity, perfumers have

formulated around the composition. For example, by having a carrier or encapsulating material for such notes such as with cyclodextrin, zeolites or starch.

Still another solution is the use of a glucosamine as described in JP 09040687. However, this compound has been found to give a very low stability in the wash/cleaning process. As a result, insufficient perfume residuality on the treated fabric and/or hard surface has been found with these glucosamine compounds.

A further solution is described in Chemical release control, Kamogawa et Al., J. Poly. Sci. Polym. Chem. Ed. Vol 20, 3121 (1982) which describe the use of amino styrene compounds condensed with aldehydes perfumes, whereby the release of the perfume is triggered by means of copolymerisation or acidification of the compound. Its use in laundry and cleaning product is however not mentioned.

The Applicant has now found that a reaction product of an amino functional polymer comprising at least one primary and/or secondary amine group, and a perfume component also fulfill such a need.

Another advantage of the compounds of the invention is their ease of manufacture rendering their use most desirable.

Summary of the invention

The present invention relates to a laundry and cleaning composition comprising a deterative ingredient and a product of reaction between an amino functional polymer comprising at least one primary and/or secondary amine group and a perfume component selected from ketone, aldehyde, and mixtures thereof, characterised in that said amino functional polymer has an Odour Intensity Index of less than that of a 1% solution of methylanthranilate in dipropylene glycol, and the product of reaction a Dry Surface Odour Index of more than 5.

In a further aspect of the invention, there is provided a method of delivering residual fragrance to a surface by means of the compound or composition of the invention.

Detailed description of the invention

I-Product of reaction between an amino functional polymer and a perfume component

An essential component of the invention is a product of reaction an amino functional polymer comprising at least one primary and/or secondary amine group and a perfume component, so called hereinafter "amine reaction product".

A- Amino functional polymer

The amino functional polymer is characterized by an Odour Intensity Index of less than that of a 1% solution of methylantranilate in dipropylene glycol.

Odour Intensity Index method

By Odour Intensity Index, it meant that the pure chemicals were diluted at 1% in Dipropylene Glycol, odor-free solvent used in perfumery. This percentage is more representative of usage levels. Smelling strips, or so called "blotters", were dipped and presented to the expert panellist for evaluation. Expert panellists are assessors trained for at least six months in odor grading and whose gradings are checked for accuracy and reproducibility versus a reference on an on-going basis. For each an amino functional polymer, the panellist was presented two blotters: one reference (Me Anthranilate, unknown from the panellist) and the sample. The panellist was asked to rank both smelling strips on the 0-5 odor intensity scale, 0 being no odor detected, 5 being very strong odor present.

Results:

The following represents Odour Intensity Index of an amino functional polymer suitable for use in the present invention and according to the above procedure. In each case, numbers are arithmetic averages among 5 expert panellists and the results are statistically significantly different at 95% confidence level:

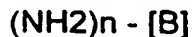
Methylantranilate 1% (reference)

3.4

1,4-bis-(3-aminopropyl) piperazine (BNPP) 1%

1.0

A general structure for the amino functional polymer containing at least one primary amine group of the present invention, is as follows:



wherein n is an index of at least 1 and B is the polymer backbone. B can optionally comprise a branching group, C and hence the amino functional polymer is of the following formula:



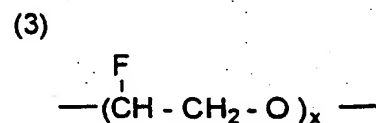
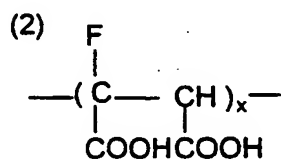
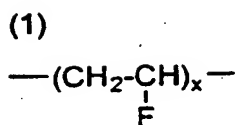
Amino functional polymer containing a secondary amine group have a structure similar to the above excepted that the polymer comprises one or more -NH- groups instead of -NH₂. Further, the polymer structure may also have one or more of both -NH₂ and -NH- groups.

The amino functional polymer of the present invention contains at least one free, unmodified primary and/or secondary amino group attached to the main chain by hydrogen substitution, or by other suitable insertion or substitution by groups referred to as R*. Also suitable is the amino functional polymer comprising an unmodified primary and/or secondary amino group present on side chain(s).

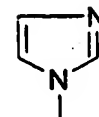
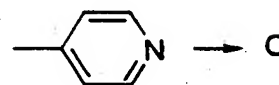
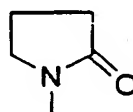
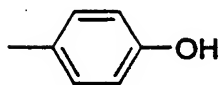
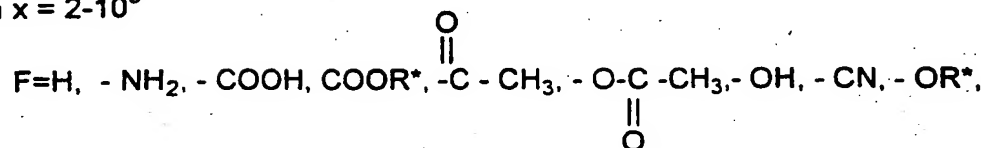
Preferably, the amino functional polymers of the present invention will comprise several amino groups, more preferably more than 10 amino groups. The amino functional polymers of the present invention will preferably present a molecular weight (MW) ranging from 150 to 2.10E6; more preferably from 400-50,000; most preferably from 600 to 40,000.

The amino functional polymer can be a linear homo-, co-polymer and optionally branched, grafted and/or cross-linked.

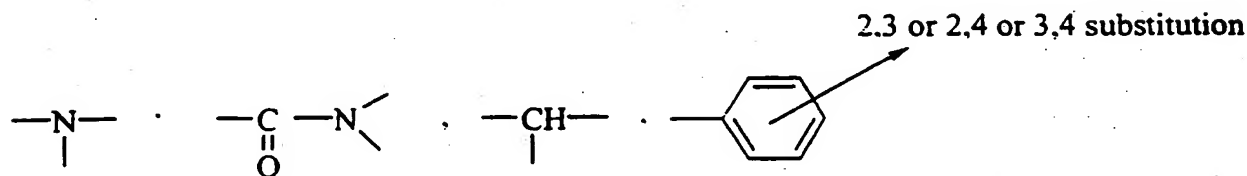
Suitable polymer backbone B for the purpose of the present invention have the following polymer units :



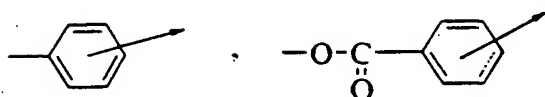
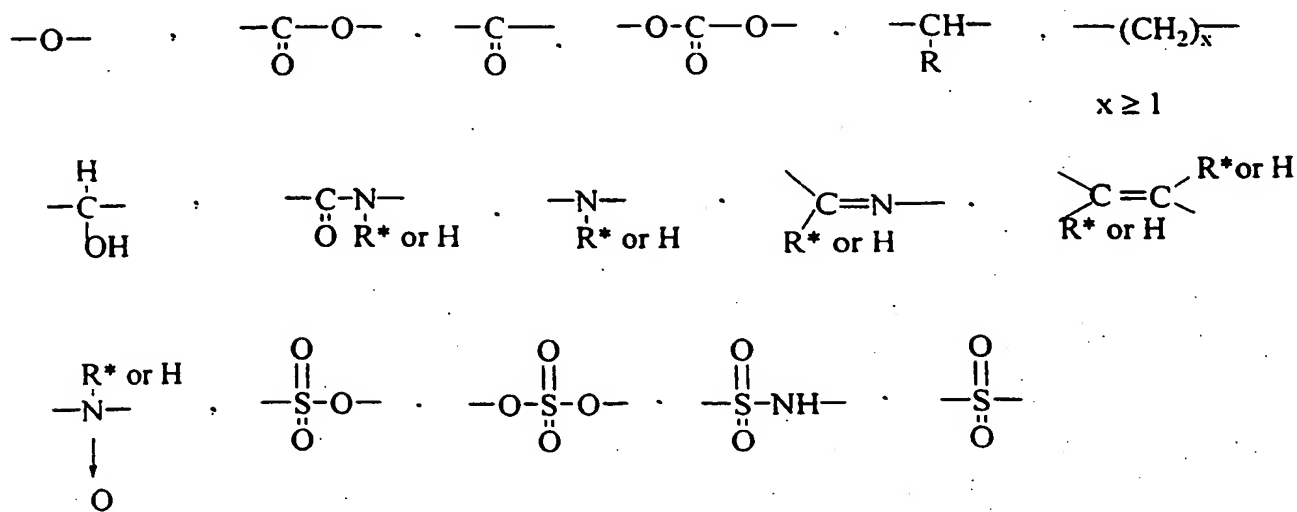
wherein $x = 2\text{--}10^5$



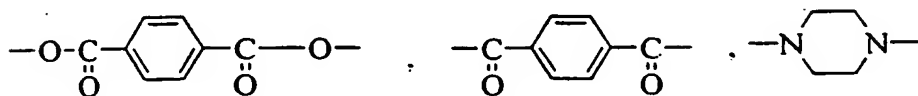
Suitable branching units C for the polymer backbone B are :



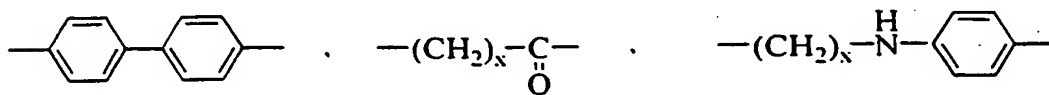
The polymer backbone B can also comprise insertion groups I such as :



The arrow indicates substitution in position 2,3 or 4



The backbone (B) can also contain several insertion groups linked together: e.g.



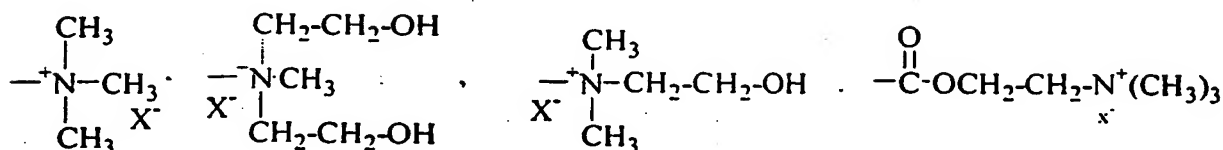
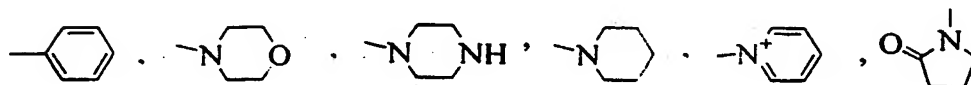
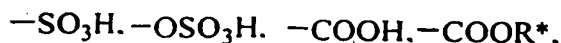
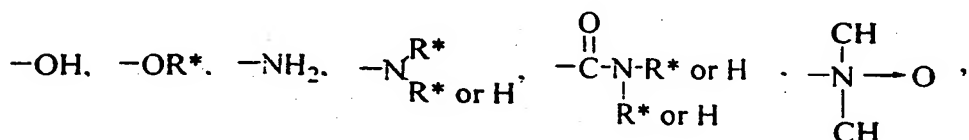
wherein $x \geq 1$.

The aminofunctional polymers of the present invention can further comprise substituents R^* in the main chain or in the side chain(s). Typically, R^* replaces an hydrogen atom. This R^* group can either be linked directly or via a linker group L to the main or side chain. Suitable linker groups L are the above mentioned insertion groups I.

R^* groups are C1 to C22 alkyl, alkenyl, alkylbenzene chain and/or their corresponding substituted derivatives. Such corresponding substituted

derivatives include alicyclic, aromatic, heteroaromatic or heterocyclic systems, either inserted in the main chain or incorporated by a substitution of an H atom in the main chain; an insertion group I in the main chain, as defined herein above and/or an end group E as defined below.

Further, the polymer backbone B and R* encompass end groups E. Typically end groups E can be an H, NH₂ groups, an aromatic, alicyclic, heteroaromatic or heterocyclic group including mono-, di-, oligo-, poly-saccharides :



wherein x⁻ is an anion like Cl⁻, Br⁻, SO₄²⁻.

In addition, the R* group can also be modified via substitution of one or more H atoms. Said substitution can either be an end group E or an insertion group I as defined above, where the insertion group is terminated by a H, E or R* group.

Preferred examples of suitable amino-functional polymers for use in the present invention are selected from the polyvinylamines, derivatives thereof, copolymer thereof, alkylene polyamine, polyaminoacid and copolymer thereof, cross-linked polyaminoacids, amino substituted polyvinylalcohol, polyoxyethylene bis amine

or bis aminoalkyl, aminoalkyl piperazine and derivatives, N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched (TPTA), and mixtures thereof.

Polyamino acid is one suitable and preferred class of amino-functional polymer. Polyaminoacids are compounds which are made up of amino acids or chemically modified amino acids. They can contain alanine, serine, aspartic acid, arginine, valine, threonine, glutamic acid, leucine, cysteine, histidine, lysine, isoleucine, tyrosine, asparagine, methionine, proline, tryptophan, phenylalanine, glutamine, glycine or mixtures thereof. In chemically modified amino acids, the amine or acidic function of the amino acid has reacted with a chemical reagent. This is often done to protect these chemical amine and acid functions of the amino acid in a subsequent reaction or to give special properties to the amino acids, like improved solubility. Examples of such chemical modifications are benzyloxycarbonyl, aminobutyric acid, butyl ester, pyroglutamic acid. More examples of common modifications of amino acids and small amino acid fragments can be found in the Bachem, 1996, Peptides and Biochemicals Catalog.

Preferred polyamino acids are polylysines, polyarginine, polyglutamine, polyasparagine, polyhistidine, polytryptophane or mixtures thereof. Most preferred are polylysines or polyamino acids where more than 50% of the amino acids are lysine, since the primary amine function in the side chain of the lysine is the most reactive amine of all amino acids.

The preferred polyamino acid has a molecular weight of 500 to 10.000.000, more preferably between 5.000 and 750.000.

The polyamino acid can be cross linked. The cross linking can be obtained for example by condensation of the amine group in the side chain of the amino acid like lysine with the carboxyl function on the amino acid or with protein cross linkers like PEG derivatives. The cross linked polyamino acids still need to have free primary and/or secondary amino groups left for reaction with the active ingredient.

The preferred cross linked polyamino acid has a molecular weight of 20.000 to 10.000.000, more preferably between 200.000 and 2.000.000.

The polyamino acid or the amino acid can be co-polymerized with other reagents like for instance with acids, amides, acyl chlorides. More specifically with aminocaproic acid, adipic acid, ethylhexanoic acid, caprolactam or mixture thereof. The molar ratio used in these copolymers ranges from 1:1 (reagent/ amino acid (lysine)) to 1:20, more preferably from 1:1 to 1:10.

The polyamino acid like polylysine can be partially ethoxylated.

Examples and supply of polyaminoacids containing lysine, arginine, glutamine, asparagine are given in the Bachem 1996, Peptides and Biochemicals catalog.

The polyaminoacid can be obtained before reaction with the active ingredient, under a salt form. For example polylysine can be supplied as polylysine hydrobromide. Polylysine hydrobromide is commercially available from Sigma, Applichem, Bachem and Fluka.

Examples of suitable amino functional polymers containing at least one primary and/or secondary amine group for the purpose of the present invention are :

- Polyvinylamine with a MW of about 300-2.10E6;
- Polyvinylamine alkoxylated with a MW of about 600, 1200 or 3000 and an thoxylation degree of 0.5;
- Polyvinylamine vinylalcohol - molar ratio 2:1, polyvinylaminevinylformamide - molar ratio 1:2 and polyvinylamine vinylformamide-molar ratio 2:1;
- Triethylenetetramine, diethylenetriamine, tetraethylenepentamine;
- Bis-aminopropylpiperazine;
- Polyamino acid (L-lysine / lauric acid in a molar ratio of 10/1), Polyamino acid (L-lysine / aminocaproic acid / adipic acid in a molar ratio of 5/5/1),), Polyamino acid (L-lysine / aminocaproic acid /ethylhexanoic acid in a molar ratio of 5/3/1) Polyamino acid (polylysine-cocaprolactam); Polylysine hydrobromide, cross-linked polylysine,
- amino substituted polyvinylalcohol with a MW ranging from 400-300,000;
- polyoxyethylene bis [amine] availabl from e.g. Sigma;
- polyoxyethylene bis [6-aminohexyl] available from e.g. Sigma;

- N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched (TPTA); and
- 1,4-bis-(3-aminopropyl) piperazine (BNPP).

Preferred amino functional polymers containing at least one primary and/or secondary amine group are :

- polyvinylamines with a MW ranging from 600, 1200, 3K, 20K, 25K or 50K;
- amino substituted polyvinylalcohol with a MW ranging from 400-300,000;
- polyoxyethylene bis [amine] available from e.g. Sigma;
- polyoxyethylene bis [6-aminohexyl] available from e.g. Sigma;
- N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched (TPTA);
- 1,4-bis-(3-aminopropyl) piperazine (BNPP);
- Polylysine hydrobromide;
- cross-linked polylysine.

Furthermore, such amino functional polymers comprising at least one primary and/or secondary amine group and the amine reaction product provide fabric appearance benefits, in particular color care and protection against fabric wear. Indeed, the appearance of fabrics, e.g., clothing, bedding, household fabrics like table linens is one of the area of concern to consumers. Indeed, upon typical consumer's uses of the fabrics such as wearing, washing, rinsing and/or tumble-drying of fabrics, a loss in the fabric appearance; which can be at least partly due to loss of color fidelity and color definition, is observed. Such a problem of color loss is even more acute after multiwash cycles. It has been found that the compositions of the present invention provide improved fabric appearance and protection against fabric wear and improved color care to laundered fabrics, especially after multiwash cycles.

Therefore, the compositions of the present invention can provide simultaneously fabric care and long lasting perfume benefits.

B-Perfume

Preferably, for the above mentioned compounds, by perfume ketone or aldehyde, it is meant any chain containing at least 1 carbon atom, preferably at least 5 carbon atoms.

A typical disclosure of suitable ketone and/or aldehydes, traditionally used in perfumery, can be found in "perfume and Flavor Chemicals", Vol. I and II, S. Arctander, Allured Publishing, 1994, ISBN 0-931710-35-5.

Perfume ketones components include components having odoriferous properties.

Preferably, for the above mentioned compounds, the perfume ketone is selected for its odor character from buccoxime; iso jasmone; methyl beta naphthyl ketone; musk indanone; tonalid/musk plus; Alpha-Damascone, Beta-Damascone, Delta-Damascone, Iso-Damascone, Damascenone, Damarose, Methyl-Dihydrojasmonate, Menthone, Carvone, Camphor, Fenchone, Alpha-Ionone, Beta-Ionone, Gamma-Methyl so-called Ionone, Fleuramone, Dihydrojasmone, Cis-Jasmone, Iso-E-Super, Methyl- Cedrenyl-ketone or Methyl-Cedrylone, Acetophenone, Methyl-Acetophenone, Para-Methoxy-Acetophenone, Methyl-Beta-Naphtyl-Ketone, Benzyl-Acetone, Benzophenone, Para-Hydroxy-Phenyl-Butanone, Celery Ketone or Livescone, 6-Isopropyldecahydro-2-naphtone, Dimethyl-Octenone, Freskomenthe, 4-(1-Ethoxyvinyl)-3,3,5,5,-tetramethyl-Cyclohexanone, Methyl-Heptenone, 2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl)-cyclopentanone, 1-(p-Menthen-6(2)-yl)-1-propanone, 4-(4-Hydroxy-3-methoxyphenyl)-2-butanone, 2-Acetyl-3,3-Dimethyl-Norbornane, 6,7-Dihydro-1,1,2,3,3-Pentamethyl-4(5H)-Indanone, 4-Damascol, Dulcinyll or Cassione, Gelsone, Hexalon, Isocyclemonone E, Methyl Cyclocitrone, Methyl-Lavender-Ketone, Orivon, Para-tertiary-Butyl-Cyclohexanone, Verdone, Delphone, Muscone, Neobutenone, Plicatone, Veloutone, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Tetrameran, Undecalactone and Gamma undecalactone.

For the above mentioned compounds, the more preferred ketones are selected for its odor character from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.

Perfume aldehyde components include components having odoriferous properties.

Preferably, for the above mentioned compounds, the perfume aldehyde is selected for its odor character from adoxal; anisic aldehyde; cymal; ethyl vanillin; florhydral; helional; heliotropin; hydroxycitronellal; koavone; lauric aldehyde; lyral; methyl nonyl acetaldehyde; P. T. buccinal; phenyl acetaldehyde; undecylenic aldehyde; vanillin; 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amylic cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl) propanal, 2-methyl-4-(2,6,6-trimethyl-2(1)-cyclohexen-1-yl) butanal, 3-phenyl-2-propenal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al, [(3,7-dimethyl-6-octenyl)oxy] acetaldehyde, 4-isopropylbenzaldehyde, 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tricyclo[5.2.1.0(2,6)]-decylidene-8)-butanal, octahydro-4,7-methano-1H-indenecarboxaldehyde, 3-ethoxy-4-hydroxy benzaldehyde, para-ethyl-alpha, alpha-dimethyl hydrocinnamaldehyde, alpha-methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxybenzaldehyde, alpha-n-hexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyl octanal, Undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)(4-methyl-3-pentenyl)-3-cyclohexen-carboxaldehyde, 1-dodecanal, 2,4-dimethyl cyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5,9-undecadienal, 2-methyl-3-(4-tertbutyl)propanal, dihydrocinnamic aldehyde, 1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carboxaldehyde, 5 or 6 methoxyhexahydro-4,7-methanoindan-1 or 2- carboxaldehyde, 3,7-dimethyloctan-1-al, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxy benzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclohexenecarboxaldehyde, 7-hydroxy-3,7-dimethyl-octanal, trans-4-decenal, 2,6-nonadienal, para-tolylacetaldehyde; 4-methylphenylacetaldehyde, 2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylene-6-octenal, phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, peony aldehyde (6,10-dimethyl-3-oxa-5,9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carboxaldehyde, 2-methyl octanal, alpha-methyl-4-(1-methyl ethyl) benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para methyl phenoxy acetaldehyde, 2-methyl-3-phenyl-2-propen-1-al, 3,5,5-trimethyl

hexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1]-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, 1-p-menthene-q-carboxaldehyde and mixtures thereof.

More preferred aldehydes are selected for its odor character from 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amyl cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Bucinal, lyral, cymal, methyl nonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof.

In the above list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention.

In another embodiment, especially suitable for the purpose of the present invention are the perfume compounds, preferably the perfume ketones or aldehydes, characterized by having a low Odor Detection Threshold. Such Odor Detection Threshold (ODT) should be lower than 1ppm, preferably lower than 10ppb - measured at controlled Gas Chromatography (GC) conditions such as described here below. This parameter refers to the value commonly used in the perfumery arts and which is the lowest concentration at which significant detection takes place that some odorous material is present. Please refer for example in "Compilation of Odor and Taste Threshold Value Data (ASTM DS 48 A)", edited by F. A. Fazzalari, International Business Machines, Hopwell Junction, NY and in Calkin et al., Perfumery, Practice and Principles, John Willey & Sons, Inc., page 243 et seq. (1994). For the purpose of the present invention, the Odor Detection Threshold is measured according to the following method :

The gas chromatograph is characterized to determine the exact volume of material injected by the syringe, the precise split ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 0.02 minutes, the sampled volume is calculated. Since the precise concentration at the detector at any point in time

is known, the mass per volume inhaled is known and hence the concentration of material. To determine the ODT of a perfume material, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is noticed. The average over all panelists determines the threshold of noticeability. The necessary amount of analyte is injected onto the column to achieve a certain concentration, such as 10 ppb, at the detector. Typical gas chromatograph parameters for determining odor detection thresholds are listed below.

GC: 5890 Series II with FID detector

7673 Autosampler

Column: J&W Scientific DB-1

Length 30 meters ID 0.25 mm film thickness 1 micron

Method:

Split Injection: 17/1 split ratio

Autosampler: 1.13 microliters per injection

Column Flow: 1.10 mL/minute

Air Flow: 345 mL/minute

Inlet Temp. 245°C

Detector Temp. 285°C

Temperature Information

Initial Temperature: 50°C

Rate: 5C/minute

Final Temperature: 280°C

Final Time: 6 minutes

Leading assumptions: 0.02 minutes per sniff

GC air adds to sample dilution

Examples of such preferred perfume components are those selected from : 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde, 1-(2,6,6-trimethyl-2-cyclohexan-1-yl)-2-buten-1-one and/or para-methoxy-acetophenone. Even more preferred are the following compounds having an ODT ≤ 10 ppb measured with the method described above : undecylenic aldehyde, undecalactone gamma, heliotropin, dodecalactone gamma, p-anisic aldehyde, para hydroxy-phenyl-butanone, cymal, benzyl acetone, ionone alpha, p.t.bucinal, damascenone, ionone beta and methyl-nonyl ketone.

Typically the level of perfume is of from 10 to 90%, preferably from 30 to 85%, more preferably from 45 to 80% by weight of the amine reaction product.

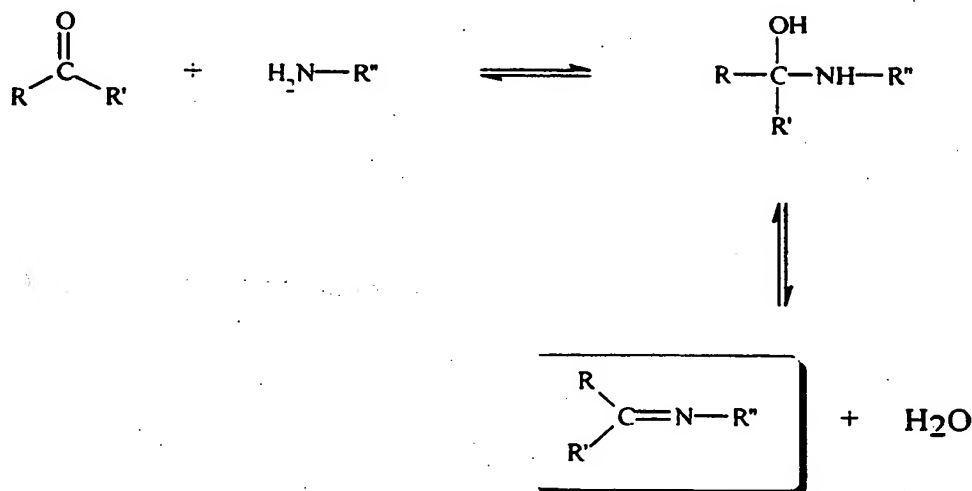
Preferred amine reaction products are those resulting from the reaction of polyaminoacid like Polylysine, BNPP, or TPTA with one or more of the following Alpha Damascone, Delta Damascone, Carvone, Hedione, Florhydral, Lilial, Heliotropine, Gamma-Methyl-Ionone and 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, and mixture thereof.

Most preferred amine reaction products are those from the reaction of BNPP or TPTA with Alpha and Delta Damascone.

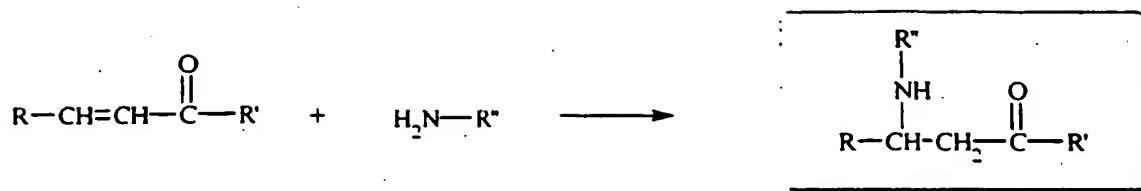
Process

Preparation of the component is made as follows in the Synthesis Examples. In general, the nitrogen analogs of ketones and aldehydes are called azomethines, Schiff bases or the more preferred name imines. These imines can easily be prepared by condensation of primary amines and carbonyl compounds by elimination of water.

A typical reaction profile is as follows:



α,β -Unsaturated ketones do not only condense with amines to form imines, but can also undergo a competitive 1,4-addition to form β -aminoketones.



By means of this simple method, compound and composition containing said compounds are made which achieve a delayed release of the active ingredient.

As can be observed, the perfume ingredient preferably needs to be present in equimolar amount to the amine function so as to enable the reaction to take place and provide the resulting amine reaction product. Of course, higher amount are not excluded and even preferred when the amine compound comprises more than one amine function.

Mechanism of release

By the present invention, a delayed release of a perfume ingredient, i.e. ketone or aldehyde is obtained. Not to be bound by theory, the release is believed to occur by the following mechanisms:

For imine compounds, the perfume components are released upon breaking down of the imine bond, leading to the release of the perfume component and of the primary amine compound. This can be achieved by either hydrolysis, photochemical cleavage, oxidative cleavage, or enzymatic cleavage.

For β -aminoketone compounds, treatment with air moisture and/or water successfully releases the perfume component and the amine compound. However, other means of release are not excluded like hydrolysis, photochemical cleavage, oxidative cleavage, or enzymatic cleavage.

Still other means of release for imine as well as β -aminoketone compounds can be considered such as by the steaming step of ironing the treated fabric, tumble-drying, and/or wearing.

Laundry and cleaning compositions

The present invention include both laundry and cleaning compositions which are typically used for laundering fabrics and cleaning hard surfaces such as

dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of perfume ketone and/or aldehyde. Accordingly, by laundry and cleaning compositions, these are to be understood to include not only detergent compositions which provide fabric cleaning benefits, but also compositions such as hard surface cleaning which provide hard surface cleaning benefit.

Preferred are those laundry compositions which result in contacting the compound of the invention with fabric.

Preferably, the amine reaction product(s) which is incorporated into such laundry and cleaning compositions provides a dry surface Odour Index of more than 5 preferably at least 10.

By Dry Surface Odour Index, it is meant that the amine reaction product(s) provides a Delta of more than 5, wherein Delta is the difference between the Odour Index of the dry surface treated with amine reaction product(s) and the Odour Index of the dry surface treated with only the perfume raw material.

Measurement method of Dry Surface Odour Index:

For the above Dry Surface Odour Index, the amine reaction product suitable for use in the present invention needs to fulfill at least one of the following two tests. Preferred amine reaction product suitable for use in the present invention fulfill both test.

1)-For fabric surface

Product preparation:

The amine reaction product is added to the unperfumed product base.

The unperfumed product base, wherein the abbreviations are as defined herein after for the examples, is as follows:

Composition	% by weight
LAS	16
NaSKS-6	6

PB1	8
TAED	2.4
Carbonate	1
Sodium Carbonate	1
HEDP	0.4
SRP1	0.2
Photobleach	0.013
Citric acid	1.0
Protease	0.3
Lipase	0.1
Cellulase	0.1
Amylase	0.3
Zeolite	3.0
TFAA	3.0
QAS1	2.5
Silicone antifoam	1.0
Misc/minors to balance to 100%	

Levels of amine reaction product are selected so as to obtain an odour grade on the dry fabric of at least 20. After careful mixing, by shaking the container in case of a liquid, with a spatula in case of a powder, the product is allowed to sit for 24 hrs.

Washing process:

The resulting product is added into the washing machine in the dosage and in the dispenser appropriate for its category. The quantity corresponds to recommended dosages made for the corresponding market products: typically between 70 and 150 g for a detergent powder or liquid via current dosing device like granulette, or ariellette. The load is composed of four bath towels (170g) using a Miele W830 washing machine at 40°C short cycle, water input :15°Hardness at a temperature of 10-18°C, and full spin of 1200rpm.

The same process is applied for the corresponding free perfume ingredient in consideration and is used as the reference. Dosages, fabric loads and washing cycles for the referenc and the sample are identical.

Drying Proc ss:

Within two hours after the end of the washing cycle, the spinned but still wet fabrics are assessed for their odors using the scale mentioned below. Afterwards, half of the fabric pieces are hung on a line for 24 hr drying, away from any possible contaminations. Unless specified, this drying takes place indoor. Ambient conditions are at temperature between 18-25C and air moisture between 50-80%. The other half is placed in a tumble drier and undergoes a full "very dry" cycle, i.e. in a Miele, Novotronic T430 set on program white-extra dry (full cycle). Tumble dry fabrics are also assessed on the next day. Fabrics are then stored in opened aluminum bags in an odor free room, and assessed again after 7 days.

Odor Evaluations:

Odor is assessed by expert panellist smelling the fabrics. A 0-100 scale is used for all fabric odor gradings. The grading scale is as follows :

- 100 = extremely strong perfume odor
- 75 = very strong perfume odor
- 50 = strong odor
- 40 = moderate perfume odor
- 30 = slight perfume odor
- 20 = weak perfume odor
- 10 = very weak perfume odor
- 0 = no odor

A difference of more than 5 grades after one day and/or 7 days between the amine reaction product and the perfume raw material is statistically significant. A difference of 10 grades or more after one day and/or 7 days represents a step-change. In other words, when a difference of grade of more than 5, preferably at least 10 is observed between the amine reaction product and the perfume raw material, after either 1 day or 7 days or both 1 day and 7 days, it can be concluded that the amine reaction product is suitable for use in the present invention, provided that the amine compound fulfill the Odour Intensity Index.

2)-For hard surface:**Product preparation:**

The perfume raw material or blend thereof is added and carefully mixed at 0.255% in the unperfumed Hard Surface Cleaner base.

The unperfumed product base, wherein the abbreviations are as defined herein after for the examples, is as follows:

Composition for hard surface test	% by weight
C12-14 EO 21	2
C12-14 EO 5	2.5
C9-11 EO 5	2.5
LAS	0.8
Na ₂ CO ₃	0.2
Citric acid	0.8
Caustic acid	0.5
Fatty acid	0.5
SCS	1.5
Water & Misc/Minors to balance to 100%	

After mixing and standing for 24 hrs, the homogeneity of the product is checked. In case of phase separation due to poor solubility of the perfume ingredient(s) an appropriate amount of Sodium p. Cymene Sulfonate or another solubilising agent is added till a homogeneous solution is obtained.

Cleaning process:

Five grams of this solution are evenly applied on the upper side of a ceramic tile (875 square cm, e.g. from Vileroy-Boch). After 1 minute the tile is rinsed with 1 liter of tap water. The tile is then placed in a vertical position for 3 minutes to allow the rinse water to drip off.

Finally, the tile is placed in a clean and aerated perspex box (38 x 40 x 32 cm) with a removable cover that has a sliding-lid (10 x 10 cm) to allow expert evaluators to smell the interior phase of the box.

The odor in the box is evaluated just after placing the tile in it (fresh reading) and after 1, 2 and 6 hours.

Odor Evaluation:

The grading scale is as follows :

50 = very strong odor

40 = strong odor

30 = moderate odor

20 = slight odor

10 = weak odor

0 = no odor

Every test includes a blanc (unperfumed Hard Surface Cleaner) and in the case of testing perfume precursor, so-called amine reaction product the corresponding free perfume ingredient is also included so that the effect of the carrier is adequately measured.

Again as for the Dry surface Odour Index method for fabrics, a difference of more than 5 grades after 1 day and/or 7 days between the amine reaction product and the perfume raw material is statistically significant. A difference of 10 grades or more after 1 day and/or 7 days represents a step-change. In other words, when a difference of grade of more than 5, preferably at least 10 is observed between the amine reaction product and the perfume raw material, after either 1 day or 7 day or both 1 day and 7 days, it can be concluded that the amine reaction product is suitable for use in the present, provided that the amine compound fulfill the Odour Intensity Index.

The amine reaction product as defined herein before is typically comprised from 0.0001% to 10%, preferably from 0.001% to 5%, and more preferably from 0.01% to 2%, by weight of the composition. Mixtures of the compounds may also be used herein.

Incorporation of the amine reaction product in the laundry and cleaning compositions can conveniently be carried out, if necessary, by conventional incorporation means, such as by spray-on, encapsulation like starch encapsulation, e.g. as described in GB1464616, dry addition, or by encapsulation in cyclodextrin. Preferably, the amine reaction product is preformed before incorporation into the laundry and cleaning compositions. In other words, the perfume component and the amino functional polymer of the

present invention are first reacted together to obtain the resulting amine reaction product as defined in the present invention and only once formed incorporated into the laundry and cleaning compositions. By being preformed before the incorporation in fully formulated composition, a better control of the compound being made is obtained. Hence, the interaction with perfume composition which may be present in fully formulated composition is avoided as well as side reaction that could occur. Further, by such means of incorporation, efficient control of the yield and purity of the compound is obtained.

Most preferably, when the laundry and cleaning composition comprises a perfume, the amine reaction product is incorporated in the composition separately from the perfume. By this means, the amine reaction product and its subsequent perfume release is more controlled.

Typically the laundry and cleaning composition comprises a detergent ingredient and further optional ingredients as described hereinafter as optional ingredients.

Detergent ingredients

Non-limiting examples of surfactants useful herein typically at levels from 1% to 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^-\text{M}^+)\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^-\text{M}^+)\text{CH}_2\text{CH}_3$ where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially x up to 7 EO ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultain s"), C₁₀-C₁₈ amine oxides, cationic surfactants and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical

examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Fully formulated laundry and cleaning compositions preferably contain, in addition to the hereinbefore described components, one or more of the following ingredients.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least 1% builder, preferably from 1% to 80%. Liquid formulations typically comprise from 5% to 50%, more typically 5% to 30%, by weight, of detergent builder. Granular formulations typically comprise from 1% to 80%, more typically from 5% to 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the

so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.0:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. 4,664,839. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in DE 2,321,001.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers usually of at least 6, the molar ratio of z to y is in the range from 1.0 to 0, and x is an integer from 0 to 264, and M is a Group IA or IIA element. e.g., Na, K, Mg, Ca with valence n.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be

naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O}$$

wherein x is from 20 to 30, especially 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. 3,128,287, U.S. 3,635,830. See also "TMS/TDS" builders of U.S. 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, pyromellitic, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in EP 0,200,263.

Other suitable polycarboxylates are disclosed in U.S. 4,144,226 and in U.S. 3,308,067. See also U.S. 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids such as oleic acid and/or its salts, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Bleaching Compounds - Bleaching Agents and Bleach Activators

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from 1% to 30%, more typically from 5% to 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from 0.1% to 60%, more typically from 0.5% to 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents like hypochlorite bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein. When hypochlorite is used, a highly preferred hypochlorite bleaching component is an alkali metal hypochlorite. Although alkali metal hypochlorites are preferred, other hypochlorite compounds may also be used herein and can be selected from calcium and magnesium hypochlorite. A preferred alkali metal hypochlorite for use herein is sodium hypochlorite.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. 4,483,781, U.S. 740,446, EP 0,133,354, and U.S. 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. 4,634,551.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from 500 micrometers to 1,000 micrometers, not more than 10% by weight of said particles being smaller than 200 micrometers and not more than 10% by weight of said particles being larger than 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. 4,915,854, and U.S. 4,412,934. The nonanoyloxybenzene sulfonate (NOBS), 3,5,5-tri-methyl hexanoyl oxybenzene sulfonate (ISONOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

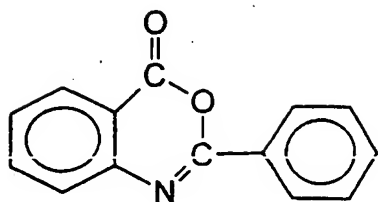
Highly preferred amido-derived bleach activators are those of the formulae:



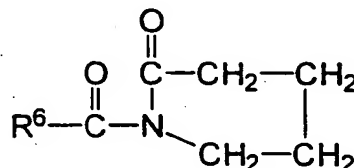
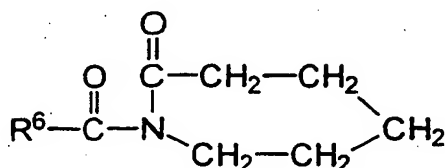
wherein R^1 is an alkyl group containing from 6 to 12 carbon atoms, R^2 is an alkylene containing from 1 to 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from 1 to 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. 4,033,718. If used, detergent compositions will typically contain from 0.025% to 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well-known in the art and include, for example, the manganese-based catalysts disclosed in U.S. 5,246,621, U.S. 5,244,594; U.S. 5,194,416; U.S. 5,114,606; and EP 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(PF_6)_2$, $Mn^{III}_2(u-O)_1(u-$

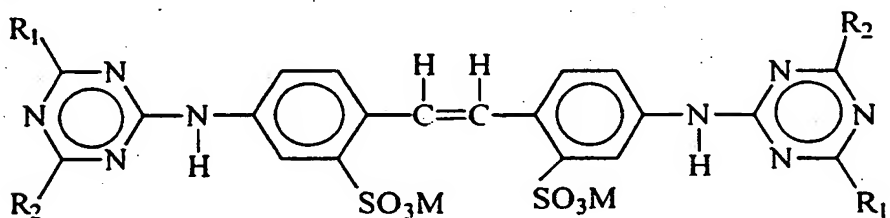
OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(ClO₄)₂, Mn^{IV}₄(u-O)₆(1,4,7-triazacyclononane)₄(ClO₄)₄, Mn^{III}Mn^{IV}₄(u-O)₁(u-OAc)₂-(1,4,7-trimethyl-1,4,7-triazacyclononane)₂(ClO₄)₃, Mn^{IV}(1,4,7-trimethyl-1,4,7-triazacyclononane)-(OCH₃)₃(PF₆), and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following US Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from 0.1 ppm to 700 ppm, more preferably from 1 ppm to 500 ppm, of the catalyst species in the laundry liquor.

Brighteners

The compositions herein can also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.001% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morpholino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the

tradename Tinopal-UNPA-GX[®] by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the rinse added compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-

stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX[®] by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX[®] by Ciba Geigy Corporation.

Soil Release Agent

In the present invention, an optional soil release agent can be added. Typical levels of incorporation in the composition are from 0% to 10%, preferably from 0.2% to 5%, of a soil release agent. Preferably, such a soil release agent is a polymer.

Soil Release agents are desirably used in fabric softening compositions of the instant invention. Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, *et al.*, issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel *et al.*, issued November 6; U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado *et al.*, issued October 31, 1989; U.S. 4,956,447, Gosselink *et al.*, issued September 11, 1990; U.S. 5,415,807 Gosselink *et al.*, issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, *et al.*

Further suitable soil release agents are described in U.S. 4,201,824, Violland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681, Ruppert *et al.*; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

Scum Dispersant

In the present invention, the premix can be combined with an optional scum dispersant, other than the soil release agent, and heated to a temperature at or above the melting point(s) of the components.

The preferred scum dispersants herein are formed by highly ethoxylating hydrophobic materials. The hydrophobic material can be a fatty alcohol, fatty acid, fatty amine, fatty acid amide, amine oxide, quaternary ammonium compound, or the hydrophobic moieties used to form soil release polymers. The preferred scum dispersants are highly ethoxylated, e.g., more than 17, preferably more than 25, more preferably more than 40, moles of ethylene oxide per molecule on the average, with the polyethylene oxide portion being from 76% to 97%, preferably from 81% to 94%, of the total molecular weight.

The level of scum dispersant is sufficient to keep the scum at an acceptable, preferably unnoticeable to the consumer, level under the conditions of use, but not enough to adversely affect softening. For some purposes it is desirable that the scum is nonexistent. Depending on the amount of anionic or nonionic detergent, etc., used in the wash cycle of a typical laundering process, the efficiency of the rinsing steps prior to the introduction of the compositions herein, and the water hardness, the amount of anionic or nonionic detergent surfactant and detergency builder (especially phosphates and zeolites) entrapped in the fabric (laundry) will vary. Normally, the minimum amount of scum dispersant should be used to avoid adversely affecting softening properties. Typically scum dispersion requires at least 2%, preferably at least 4% (at least 6% and preferably at least 10% for maximum scum avoidance) based upon the level of softener active. However, at levels of 10% (relative to the softener material) or more, one risks loss of softening efficacy of the product especially when the fabrics contain high proportions of nonionic surfactant which has been absorbed during the washing operation.

Preferred scum dispersants are: Brij 700®; Varonic U-250®; Genapol T-500®, Genapol T-800®; Plurafac A-79®; and Neodol 25-50®.

Bactericides

Examples of bactericides used in the compositions of this invention include glutaraldehyde, formaldehyde, 2-bromo-2-nitro-propane-1,3-diol sold by Inolex Chemicals, located in Philadelphia, Pennsylvania, under the trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon 1 to 1,000 ppm by weight of the agent.

Perfume

The present invention can contain any detergent compatible perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such

as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpineol; 3,7-dimethyl-*cis*-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-*trans*-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecenyl propionate; tricyclodecenyl acetate; anisaldehyde; 2-methyl-2-(para-isopropylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methylether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate; methylphenylcarbonyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecandioic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; isohexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; olibanum resinoid; labdanum; vetivert; copaiba balsam; fir balsam;

and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.

More examples of perfume components are geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopyl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbinyl methylphenylcarbinyl acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert-butylphenyl)-propanal; 2-methyl-3-(p-isopropylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentylcyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methylether; isolongifolanone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionones; irones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

Chelating Agents

The compositions and processes herein can optionally employ one or more copper and/or nickel chelating agents ("chelators"). Such water-soluble chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined. The whiteness and/or brightness of fabrics are substantially improved or restored by such chelating agents and the stability of the materials in the compositions are improved. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetra-aminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

Preferred chelating agents include DETMP, DETPA, NTA, EDDS and mixtures thereof.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the fabric care compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Crystal growth inhibitor component

The compositions of the present invention can further contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the compositions.

By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

The organo diphosphonic acid is preferably a C₁-C₄ diphosphonic acid, more preferably a C₂ diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

Still useful herein as crystal growth inhibitor are the organic monophosphonic acid

Organo monophosphonic acid or one of its salts or complexes is also suitable for use herein as a CGI.

By organo monophosphonic acid it is meant herein an organo monophosphonic acid which does not contain nitrogen as part of its chemical structure. This

definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrants.

The organo monophosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred.

A preferred organo monophosphonic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer under the tradename of Bayhibit.

Enzyme

The compositions and processes herein can optionally employ one or more enzymes such as lipases, proteases, cellulase, amylases and peroxidases. A preferred enzyme for use herein is a cellulase enzyme. Indeed, this type of enzyme will further provide a color care benefit to the treated fabric. Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307 discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. Other suitable cellulases are also disclosed in WO 91/17243 to Novo, WO 96/34092, WO 96/34945 and EP-A-0,739,982. In practical terms for current commercial preparations, typical amounts are up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. In the particular cases where activity of the enzyme preparation can be defined otherwise such as with cellulases, corresponding activity units are preferred (e.g. CEVU or cellulase Equivalent Viscosity Units). For instance, the compositions of the present invention can contain cellulase enzymes at a level equivalent to an activity from 0.5 to 1000 CEVU/gram of

composition. Cellulase enzyme preparations used for the purpose of formulating the compositions of this invention typically have an activity comprised between 1,000 and 10,000 CEVU/gram in liquid form, around 1,000 CEVU/gram in solid form.

Clay

The compositions of the invention may preferably contain a clay, preferably present at a level of from 0.05% to 40%, more preferably from 0.5% to 30%, most preferably from 2% to 20% by weight of the composition. For clarity, it is noted that the term clay mineral compound, as used herein, excludes sodium aluminosilicate zeolite builder compounds, which however, may be included in the compositions of the invention as optional components.

One preferred clay may be a bentonite clay. Highly preferred are smectite clays, as for example disclosed in the US Patents No.s 3,862,058 3,948,790, 3,954,632 and 4,062,647 and European Patents No.s EP-A-299,575 and EP-A-313,146 all in the name of the Procter and Gamble Company.

The term smectite clays herein includes both the clays in which aluminium oxide is present in a silicate lattice and the clays in which magnesium oxide is present in a silicate lattice. Typical smectite clay compounds include the compounds having the general formula $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$ and the compounds having the general formula $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Smectite clays tend to adopt an expandable three layer structure.

Specific examples of suitable smectite clays include those selected from the classes of the montmorillonites, hectorites, volchonskoites, nontronites, saponites and sauconites, particularly those having an alkali or alkaline earth metal ion within the crystal lattice structure. Sodium or calcium montmorillonite are particularly preferred.

Suitable smectite clays, particularly montmorillonites, are sold by various suppliers including English China Clays, Laviosa, Georgia Kaolin and Colin Stewart Minerals.

Clays for use herein preferably have a particle dimension of from 10nm to 800nm more preferably from 20nm to 500 nm, most preferably from 50nm to 200 nm.

Particles of the clay mineral compound may be included as components of agglomerate particles containing other detergent compounds. Where present as such components, the term "largest particle dimension" of the clay mineral compound refers to the largest dimension of the clay mineral component as such, and not to the agglomerated particle as a whole.

Substitution of small cations, such as protons, sodium ions, potassium ions, magnesium ions and calcium ions, and of certain organic molecules including those having positively charged functional groups can typically take place within the crystal lattice structure of the smectite clays. A clay may be chosen for its ability to preferentially absorb one cation type, such ability being assessed by measurements of relative ion exchange capacity. The smectite clays suitable herein typically have a cation exchange capacity of at least 50 meq/100g. U.S. Patent No. 3,954,632 describes a method for measurement of cation exchange capacity.

The crystal lattice structure of the clay mineral compounds may have, in a preferred execution, a cationic fabric softening agent substituted therein. Such substituted clays have been termed 'hydrophobically activated' clays. The cationic fabric softening agents are typically present at a weight ratio, cationic fabric softening agent to clay, of from 1:200 to 1:10, preferably from 1:100 to 1:20. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

A preferred commercially available "hydrophobically activated" clay is a bentonite clay containing approximately 40% by weight of a dimethyl ditallow quaternary ammonium salt sold under the tradename Claytone EM by English China Clays International.

In a highly preferred embodiment of the invention, the clay is present in an intimate mixture or in a particle with a humectant and a hydrophobic compound,

preferably a wax or oil, such as paraffin oil. Preferred humectants are organic compounds, including propylene glycol, ethylene glycol, dimers or trimers of glycol, most preferably glycerol. The particle is preferably an agglomerate. Alternatively, the particle may be such that the wax or oil and optionally the humectant form an encapsulate on the clay or alternatively, the clay be a encapsulate for the wax or oil and the humectant. It may be preferred that the particle comprises an organic salt or silica or silicate.

However, in another embodiment of the invention, the clay is preferably mixed with one or more surfactants and optionally builders and optionally water, in which case the mixture is preferably subsequently dried. Preferably, such a mixture is further processed in a spray-drying method to obtain a spray dried particle comprising the clay.

It may be preferred that the flocculating agent is also comprised in the particle or granule comprising the clay.

It may also be preferred that the intimate mixture comprises a chelating agent.

Flocculating agent

The compositions of the invention may contain a clay flocculating agent, preferably present at a level of from 0.005% to 10%, more preferably from 0.05% to 5%, most preferably from 0.1% to 2% by weight of the composition.

The clay flocculating agent functions such as to bring together the particles of clay compound in the wash solution and hence to aid their deposition onto the surface of the fabrics in the wash. This functional requirement is hence different from that of clay dispersant compounds which are commonly added to laundry detergent compositions to aid the removal of clay soils from fabrics and enable their dispersion within the wash solution.

Preferred as clay flocculating agents herein are organic polymeric materials having an average weight of from 100,000 to 10,000,000, preferably from 150,000 to 5,000,000, more preferably from 200,000 to 2,000,000.

Suitable organic polymeric materials comprise homopolymers or copolymers containing monomeric units selected from alkylene oxide, particularly ethylene oxide, acrylamide, acrylic acid, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Homopolymers of, on particular, ethylene oxide, but also acrylamide and acrylic acid are preferred.

European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe preferred organic polymeric clay flocculating agents for use herein.

The weight ratio of clay to the flocculating polymer is preferably from 1000:1 to 1:1, more preferably from 500:1 to 1:1, most preferably from 300:1 to 1:1, or even more preferably from 80:1 to 10:1, or in certain applications even from 60:1 to 20:1.

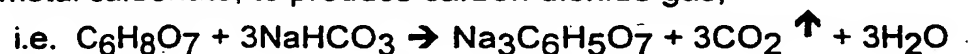
Inorganic clay flocculating agents are also suitable herein, typical examples of which include lime and alum.

The flocculating agent is preferably present in a detergent base granule such as a detergent agglomerate, extrudate or spray-dried particle, comprising generally one or more surfactants and builders.

Effervescent

Effervescent means may also be optionally used in the compositions of the invention.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,



Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

Carbonate salts

Suitable alkali and/ or earth alkali inorganic carbonate salts herein include carbonate and hydrogen carbonate of potassium, lithium, sodium, and the like amongst which sodium and potassium carbonate are preferred. Suitable bicarbonates to be used herein include any alkali metal salt of bicarbonate like lithium, sodium, potassium and the like, amongst which sodium and potassium bicarbonate are preferred. However, the choice of carbonate or bicarbonate or mixtures thereof may be made depending on the pH desired in the aqueous medium wherein the granules are dissolved. For example where a relative high pH is desired in the aqueous medium (e.g., above pH 9.5) it may be preferred to use carbonate alone or to use a combination of carbonate and bicarbonate wherein the level of carbonate is higher than the level of bicarbonate. The inorganic alkali and/ or earth alkali carbonate salt of the compositions of the invention comprises preferably a potassium or more preferably a sodium salt of carbonate and/ or bicarbonate. Preferably, the carbonate salt comprises sodium carbonate, optionally also a sodium bicarbonate.

The inorganic carbonate salts herein are preferably present at a level of at least 20% by weight of the composition. Preferably they are present at a level of at least 23% or even 25% or even 30% by weight, preferably up to about 60% by weight or more preferably up to 55% or even 50% by weight.

They may be added completely or partially as separate powdered or granular component, as co-granules with other detergent ingredients, for example other salts or surfactants. In solid detergent compositions of the invention, they may also completely or partially be present in detergent granules such as agglomerates or spray dried granules.

In one embodiment of the invention, an effervescence source is present, preferably comprising an organic acid, such as carboxylic acids or aminoacids, and a carbonate. Then it may be preferred that part or all of the carbonate salt herein is premixed with the organic acid, and thus present in an separate granular component.

Preferred effervescent source are selected from compressed particles of citric acid and carbonate optionally with a binder; and particle of carbonate,

bicarbonat and malic or maleic acid in weight ratios of 4:2:4. The dry add form of citric acid and carbonate are preferably used.

The carbonate may have any particle size. In one embodiment, in particular when the carbonate salt is present in a granule and not as separately added compound, the carbonate salt has preferably a volume median particle size from 5 to 375 microns, whereby preferably at least 60%, preferably at least 70% or even at least 80% or even at least 90% by volume, has a particle size of from 1 to 425 microns. More preferably, the carbon dioxide source has a volume median particle size of 10 to 250, whereby preferably at least 60 %, or even at least 70% or even at least 80% or even at least 90% by volume, has a particle size of from 1 to 375 microns; or even preferably a volume median particle size from 10 to 200 microns, whereby preferably at least 60 %, preferably at least 70% or even at least 80% or even at least 90% by volume, has a particle size of from 1 to 250 microns.

In particular when the carbonate salt is added as separate component, so to say 'dry-added' or admixed to the other detergent ingredients, the carbonate may have any particle size, including the above specified particle sizes, but preferably at least an volume average particle size of 200 microns or even 250 microns or even 300 microns.

It may be preferred that the carbon dioxide source of the required particle size is obtained by grinding a larger particle size material, optionally followed by selecting the material with the required particle size by any suitable method.

Whilst percarbonate salts may be present in the compositions of the invention as a bleaching agent, they are not included in the carbonate salts as defined herein

Other preferred optional ingredients include enzyme stabilisers, polymeric soil release agents, materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process (i.e., dye transfer inhibiting agents), polymeric dispersing agents, suds suppressors, optical brighteners or other brightening or whitening agents, anti-static agents, other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations and solid fillers for bar compositions.

Form of the composition

The composition of the invention may take a variety of physical form including liquid, gel, foam in either aqueous or non-aqueous form, granular and tablet forms.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

Granular detergents can be prepared, for example, by spray-drying (final product density 520 g/l) or agglomerating (final product density above 600 g/l) the Base Granule. The remaining dry ingredients can then be admixed in granular or powder form with the Base Granule, for example in a rotary mixing drum, and the liquid ingredients (e.g., nonionic surfactant and perfume) can be sprayed on.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well-known to those skilled in the art.

When in a liquid form, the composition may also be dispensed by a dispensing means such as a spray dispenser, or aerosol dispenser.

Spray Dispenser

The present invention also relates to such compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of fabric articles and/or surfaces with said compositions containing the amine reaction product and other ingredients (examples are cyclodextrins,

polysaccharides, polymers, surfactant, perfume, softener) at a level that is effective, yet is not discernible when dried on the surfaces. The spray dispenser comprises manually activated and non-manual powered (operated) spray means and a container containing the treating composition. Typical disclosure of such spray dispenser can be found in WO 96/04940 page 19 line 21 to page 22 line 27. The articles of manufacture preferably are in association with instructions for use to ensure that the consumer applies sufficient ingredient of the composition to provide the desired benefit. Typical compositions to be dispensed from a sprayer contain a level of amine reaction product of from about 0.01% to about 5%, preferably from about 0.05% to about 2%, more preferably from about 0.1% to about 1%, by weight of the usage composition.

Method of use

The composition of the invention are suitable for use in any step of the domestic treatment, that is a pre-treatment composition, as a wash additive, as a composition suitable for use in the laundry and cleaning process. Obviously, multiple application can be made such as treating the fabric with a pre-treatment composition of the invention and thereafter with the composition suitable for use in the laundry process.

Also provided herein is a method for providing a delayed release of an active ketone or aldehyde which comprises the step of contacting the surface to be treated with a compound or composition of the invention, and thereafter contacting the treated surface with a material, preferably an aqueous medium like moisture or any other means susceptible of releasing the perfume from the amine reaction product.

By "surface", it is meant any surface onto which the compound can deposit. Typical examples of such material are fabrics, hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of a perfume ketone and/or aldehyde such as that with litter like animal litter. Preferably, the surface is selected from a fabric, a tile, a ceramic; more preferably is a fabric.

By "delayed release" is meant release of the active component (.g perfume) over a longer period of time than by the use of the active (.g., perfume) itself.

Abbreviations used in the following laundry and cleaning composition Examples

In the laundry and cleaning compositions, the abbreviated component identifications have the following meanings:

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C ₁₁₋₁₃ alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
CxyAS	:	Sodium C _{1x} - C _{1y} alkyl sulfate
C46SAS	:	Sodium C ₁₄ - C ₁₆ secondary (2,3) alkyl sulfate
CxyEzS	:	Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide
CxyEz	:	C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
QAS	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄
QAS 1	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ - C ₁₁
APA	:	C ₈ - C ₁₀ amido propyl dimethyl amine
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
STS	:	Sodium toluene sulphonate
CFAA	:	C ₁₂ -C ₁₄ (coco) alkyl N-methyl glucamide
TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
TSPP	:	Tetrasodium pyrophosphate
Zeolite A	:	Hydrated sodium aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ ·27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
NaSKS-6	:	Crystalline layered silicate of formula δ- Na ₂ Si ₂ O ₅
Citric acid	:	Anhydrous citric acid
Borate	:	Sodium borate

Carbonate	:	Anhydrous sodium carbonate with a particle size between 200µm and 900µm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm
Silicate	:	Amorphous sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O} = 2.0:1$)
Sulfate	:	Anhydrous sodium sulfate
Mg sulfate	:	Anhydrous magnesium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
MA/AA (1)	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	:	Sodium carboxymethyl cellulose
Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
Protease	:	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
Protease I	:	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
Alcalase	:	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
Lipase	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase

Lipase (1)	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
Endolase	:	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Percarbonate	:	Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt
NAC-OBS	:	(6-nonamidocaproyl) oxybenzene sulfonate
TAED	:	Tetraacetylenethylenediamine
DTPA	:	Diethylene triamine pentaacetic acid
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
Photoactivated bleach (1)	:	Sulfonated zinc phthlocyanine encapsulated in dextrin soluble polymer
Photoactivated bleach (2)	:	Sulfonated alumino phthlocyanine encapsulated in dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate
HEDP	:	1,1-hydroxyethane diphosphonic acid
PEGx	:	Polyethylene glycol, with a molecular weight of x (typically 4,000)
PEO	:	Polyethylene oxide, with an average molecular weight of 50,000
TEPAE	:	Tetraethylenepentaamine ethoxylate
PVI	:	Polyvinyl imidosole, with an average molecular weight of 20,000

PVP	:	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
PVNO	:	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
QEA	:	$\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3) - \text{N}^+ - \text{C}_6\text{H}_{12} - \text{N}^+ - (\text{CH}_3) \text{bis}((\text{C}_2\text{H}_5\text{O}) - (\text{C}_2\text{H}_4\text{O}))_n$, wherein $n =$ from 20 to 30
SRP 1	:	Anionically end capped poly esters
SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
PEI	:	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
Opacifier	:	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
Wax	:	Paraffin wax
PA30	:	Polyacrylic acid of average molecular weight of between about 4,500 - 8,000.
480N	:	Random copolymer of 7:3 acrylate/methacrylate, average molecular weight about 3,500.
Polygel/carbopol	:	High molecular weight crosslinked polyacrylates.
Metasilicate	:	Sodium metasilicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio = 1.0).
Nonionic	:	C ₁₃ -C ₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
Neodol 45-13	:	C ₁₄ -C ₁₅ linear primary alcohol ethoxylate, sold by Shell Chemical CO.
MnTACN	:	Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.
PAAC	:	Pentaamine acetate cobalt(III) salt.

Paraffin	:	Paraffin oil sold under the tradename Winog 70 by Wintershall.
NaBz	:	Sodium benzoate.
BzP	:	Benzoyl Peroxide.
SCS	:	Sodium cumene sulphonate.
BTA	:	Benzotriazole.
pH	:	Measured as a 1% solution in distilled water at 20°C.
ARP1	:	Amine reaction product of 1,4-bis-(3-aminopropyl)-piperazine with α -Damascone as made from Synthesis example I
ARP2	:	Amine reaction product of N,N'bis(aminopropyl)1,3-propanediamine with δ -Damascone as made from Synthesis example II
ARP3	:	Amine reaction product of polyvinylamine MW1200 with α -Damascone as made from Synthesis example III
Clay I	:	Bentonite clay
Clay II	:	Smectite clay
Flocculating agent I:	:	polyethylene oxide of average molecular weight of between 200,000 and 400,000
Flocculating agent II:	:	polyethylene oxide of average molecular weight of between 400,000 and 1,000,000
Flocculating agent III:	:	polymer of acrylamide and/ or acrylic acid of average molecular weight of 200,000 and 400,000
DOBS:	:	Decanoyl oxybenzene sulfonate in the form of the sodium salt
SRP 3	:	Polysaccharide soil release polymer
SRP 4	:	Nonionically end capped poly esters

The following are synthesis examples of compounds as defined in the present invention:

I-Synthesis of 1,4-bis-(3-aminopropyl)-piperazin with α -Damascon

In order to substitute both primary amine groups with a perfume, 2eq of perfume were used for 1eq of amino functional polymer. To an ice cooled stirred solution

of 1mmol of α -Damascone in 6 mL EtOH and molecular sieves (4Å, 20 g), 0.5eq of 1,4-bis-(3-aminopropyl)-piperazine was added via an addition funnel. The reaction mixture was stirred under nitrogen atmosphere and protected from light. After the disappearance of the absorption peak from the NMR spectrum of the free perfume raw material (from 3 to 16 hours), the mixture was filtrated and the solvent was removed by vacuum distillation. The yield of β -aminoketone formation is about 90%.

Similar results were obtained where the α -Damascone was replaced by Tripal, vertocitral, bourgeonal, or citronellal. In these instances, Schiff-bases are formed.

II-Synthesis of N,N'-bis(3-aminopropyl)-1,3-propanediamine with δ -Damascone

To an ice cooled solution of 1 mmol of δ -Damascone in 30 mL EtOH and molecular sieves (4Å, 5 g), 0.5eq of the N,N'-bis(3-aminopropyl)-1,3-propanediamine was added. The reaction was stirred under nitrogen atmosphere and protected from light. After 1 day, the molecular sieves and the solvent were removed by filtration and vacuum distillation respectively. β -Aminoketone were obtained in a 85 to 90% yield.

Similar results were obtained where the δ -Damascone was replaced by Tripal, vertocitral, bourgeonal, or citronellal. In these instances, Schiff-bases are formed.

III-Synthesis of Polyvinylamine of MW1200 with α -Damascone

The following ingredients were mixed together : 0.6g of Sodium sulfate with 0.3g of polyvinylamine MW 1200 in a 10% aqueous solution and 0.3g α -Damascone. The reaction was completed after 18 days at room temperature in the dark.

Similar results were obtained where the α -Damascone was replaced by Tripal, or citral. In these instances, Schiff-bases are formed.

In the following formulation examples all levels are quoted as % by weight of the composition unless otherwise stated, and incorporation of the amine reaction

product so called herein after "ARP" in the fully formulated composition is carried out by dry addition (d), spray on (s), encapsulation in starch (es) as described in GB-1,464,616 or cyclodextrin (ec) or as is in the composition as defined herein before. The term in bracket for the ARP in the formulation examples refers to the means of incorporation. When none is provided, the incorporation is made as it is. The levels given for the ARP, whether processed or not, refer to the level of ARP as is and not to the processed ARP.

Example 1

The following high density granular laundry detergent compositions were prepared in accord with the invention:

	A	B	C	D	E	F	G
LAS	8.0	8.0	8.0	2.0	6.0	6.0	5.0
TAS	-	0.5	-	0.5	1.0	0.1	1.5
C46(S)AS	2.0	2.5	-	-	-	-	-
C25AS	-	-	-	7.0	4.5	5.5	2.5
C68AS	2.0	5.0	7.0	-	-	-	0.2
C25E5	-	-	3.4	10.0	4.6	4.6	2.6
C25E7	3.4	3.4	1.0	-	-	-	-
C25E3S	-	-	-	2.0	5.0	4.5	0.5
QAS	-	0.8	-	-	-	-	-
QAS (I)	-	-	-	0.8	0.5	1.0	1.5
Zeolite A	18.1	18.0	14.1	18.1	20.0	18.1	16.2
Citric acid	-	-	-	2.5	-	2.5	1.5
Carbonate	13.0	13.0	27.0	10.0	10.0	13.0	20.6
SKS-6	-	-	-	10.0	-	10.0	4.3
Silicate	1.4	1.4	3.0	0.3	0.5	0.3	-
Citrate	-	1.0	-	3.0	-	-	1.4
Sulfate	26.1	26.1	26.1	6.0	-	-	-
Mg sulfate	0.3	-	-	0.2	-	0.2	0.03

	A	B	C	D	E	F	G
MA/AA	0.3	0.3	0.3	4.0	1.0	1.0	0.6
CMC	0.2	0.2	0.2	0.2	0.4	0.4	0.3
PB4	9.0	9.0	5.0	-	-	-	-
Percarbonate	-	-	-	-	18.0	18.0	9.0
TAED	1.5	0.4	1.5	-	3.9	4.2	3.2
NAC-OBS	-	2.0	1.0	-	-	-	-
DTPMP	0.25	0.25	0.25	0.25	-	-	-
SRP 2	-	-	-	0.2	-	0.2	-
EDDS	-	0.25	0.4	-	0.5	0.5	0.1
TFAA	-	-	-	-	-	-	1.1
CFAA	-	1.0	-	2.0	-	-	-
HEDP	0.3	0.3	0.3	0.3	0.4	0.4	0.3
QEA	-	-	-	0.2	-	0.5	-
Protease I	-	-	0.26	1.0	-	-	0.3
Protease	0.26	0.26	-	-	1.5	1.0	-
Cellulase	0.3	-	-	0.3	0.3	0.3	0.3
Amylase	0.1	0.1	0.1	0.4	0.5	0.5	0.1
Lipase (1)	0.3	-	-	0.5	0.5	0.5	0.1
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	-	20 ppm	20 ppm	20 ppm
PVNO/PVP VI	-	-	-	0.1	-	-	-
Brightener 1	0.09	0.09	0.09	-	0.09	0.09	0.01
Brightener 2	-	-	-	-	-	-	0.09
Perfume spray on	0.3	0.3	0.3	0.4	0.4	0.4	0.4

	A	B	C	D	E	F	G
ARP 1	0.08(d)	0.1(es)	-	-	0.1(d)	0.05(ec)	-
ARP 2	-	-	0.08(s)	0.1(ec)	0.1(s)	-	-
ARP 3 (es)	-	-	-	-	-	-	0.4
Silicone antifoam	0.5	0.5	0.5	-	0.3	0.3	0.3
Clay II	0.5	0.5	0.5	-	0.3	0.3	12.0
Flocculating agent I	0.5	0.5	0.5	-	0.3	0.3	0.3
Glycerol	0.5	0.5	0.5	-	0.3	0.3	0.6
Wax	0.5	0.5	0.5	-	0.3	0.3	0.4
Misc/minors to 100%							
Density in g/litre	850	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions A to F of particular utility under European machine wash conditions were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	5.5	7.5	5.0	5.0	6.0	7.0
TAS	1.25	1.86	-	0.8	0.4	0.3
C24AS/C25AS	-	2.24	5.0	5.0	5.0	2.2
C25E3S	-	0.76	1.0	1.5	3.0	1.0
C45E7	3.25	-	-	-	-	3.0
TFAA	-	-	2.0	-	-	-
C25E5	-	5.5	-	-	-	-
QAS	0.8	-	-	-	-	-
QAS II	-	0.7	1.0	0.5	1.0	0.7
STPP	19.7	-	-	-	-	-
Zeolit A	-	19.5	25.0	19.5	20.0	17.0

	A	B	C	D	E	F
NaSKS-6/citric acid (79:21)	-	10.6	-	10.6	-	-
NaSKS-6	-	-	9.0	-	10.0	10.0
Carbonate	6.1	21.4	9.0	10.0	10.0	18.0
Bicarbonate	-	2.0	7.0	5.0	-	2.0
Silicate	6.8	-	-	0.3	0.5	-
Citrate	-	-	4.0	4.0	-	-
Sulfate	39.8	-	-	5.0	-	12.0
Mg sulfate	-	-	0.1	0.2	0.2	-
MA/AA	0.5	1.6	3.0	4.0	1.0	1.0
CMC	0.2	0.4	1.0	1.0	0.4	0.4
PB4	5.0	12.7	-	-	-	-
Percarbonate	-	-	-	-	18.0	15.0
TAED	0.5	3.1	-	-	5.0	-
NAC-OBS	1.0	3.5	-	-	-	2.5
DTPMP	0.25	0.2	0.3	0.4	-	0.2
HEDP	-	0.3	-	0.3	0.3	0.3
QEA	-	-	1.0	1.0	1.0	-
Protease I	-	-	-	0.5	1.2	-
Protease	0.26	0.85	0.9	1.0	-	0.7
Lipase (1)	0.15	0.15	0.3	0.3	0.3	0.2
Cellulase	0.28	0.28	0.2	0.2	0.3	0.3
Amylase	0.1	0.1	0.4	0.4	0.6	0.2
PVNO/PVPVI	-	-	0.2	0.2	-	-
PVP	0.9	1.3	-	-	-	0.9
SRP 1	-	-	0.2	0.2	0.2	-
Photoactivated bleach (1) in ppm	15	27	-	-	20	20
Photoactivated bleach (2) in ppm	15	-	-	-	-	-
Brightener 1	0.08	0.19	-	-	0.09	0.15
Brightener 2	-	0.04	-	-	-	-
Perfume	0.3	0.3	0.4	0.3	0.4	0.3
ARP1	0.1(d)	1.0(d)	-	-	-	0.1(es)

	A	B	C	D	E	F
ARP2	-	-	0.04(s)	0.08(ec)	0.1(d)	0.1(es)
Silicone antifoam	0.5	2.4	0.3	0.5	0.3	2.0
Minors/misc to 100%						
Density in g/litre	750	750	750	750	750	750

Example 3

The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.

	A	B	C	D
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	4.0	6.0	13.0	-
MA/AA	1.0	4.0	6.0	2.0
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
Spray on				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	1.0
EDDS	0.3	-	-	-
Sulfate	2.0	3.0	5.0	10.0

	A	B	C	D
Carbonate	6.0	13.0	15.0	14.0
Citric acid	2.5	-	-	2.0
QAS II	0.5	-	-	0.5
SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-
PB4	-	18.0	10.0	21.5
TAED	2.0	2.0	-	2.0
NAC-OBS	3.0	2.0	4.0	-
Protease	1.0	1.0	1.0	1.0
Lipase	-	0.4	-	0.2
Lipase (1)	0.4	-	0.4	-
Amylase	0.2	0.2	0.2	0.4
Brightener 1	0.05	-	-	0.05
ARP3	0.03	0.1(es)	1.0	0.1 0.05(ec)
Misc/minor to 100%				

Example 4

The following granular detergent formulations were prepared in accord with the invention.

	A	B	C	D	E	F
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA (1)	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0

	A	B	C	D	E	F
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
ARP2	0.1(s)	0.05(s)	-	-	-	-
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (water etc)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS (I)	-	-	-	-	1.0	-
Citric acid	-	-	-	-	2.0	-
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5

	A	B	C	D	E	F
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-
ARP2	0.1	0.2	0.04(d)	0.02	0.01(es)	0.02(es)
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
Misc/minors to 100%						

	G	H	I	J
Blown powder				
Clay I or II	7.0	10.0	6.0	2.0
LAS	16.0	5.0	11.0	6.0
TAS	-	5.0	-	2.0
Zeolite A	-	20.0	-	10.0
STPP	24.0	-	14.0	-
Sulfate	-	2.0	-	-
MA/AA	-	2.0	1.0	1.0
Silicate	4.0	7.0	3.0	-
CMC	1.0	-	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	10.0	10.0	20.0	-
DTPMP	0.4	0.4	0.2	-
Spray on				
Brightener 1	0.02	-	-	0.02
C45E7 or E9	-	-	2.0	1.0
C45E3 or E4	-	-	2.0	4.0
Perfume	0.5	-	0.5	0.2
Silicone antifoam	0.3	-	-	-
Dry additives				
Flocculating agent I or II	0.3	1.0	1.0	0.5

QEA	-	-	-	1.0
HEDP/ EDDS	0.3	-	-	-
Sulfate	2.0	-	-	-
Carbonate	20.0	13.0	15.0	24.0
Citric acid	2.5	-	-	2.0
QAS	-	-	0.5	0.5
NaSKS-6	3.5	-	-	5.0
Percarbonate	-	-	-	9.0
PB4	-	-	5.0	-
NOBS	-	-	-	1.3
TAED	-	-	2.0	1.5
Protease	1.0	1.0	1.0	1.0
Lipase	-	0.4	-	0.2
Amylase	0.2	0.2	0.2	0.4
Brightener 2	0.05	-	-	0.05
Perfume	1.0	0.2	0.5	0.3
Speckle	1.2	0.5	2.0	-
ARP1	0.08	1.5 (d)	0.2	0.05
ARP2	3.0(d)	0.6	0.2	0.1
Misc/minor to 100%				

Example 5

The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing, according to the present invention were prepared:

	A	B	C
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerat s			
C45AS	-	-	11.0

	A	B	C
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
ARP2	0.08(s)	-	-
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
ARP1	0.05	0.08	0.1(es)
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sulfate	0.0	9.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	700	700	700

Example 6

The following granular detergent formulations were prepared in accord with the invention.

	A	B	C	D
Base granule				
Zeolite A	30.0	22.0	24.0	10.0
Sulfate	10.0	5.0	10.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
ARP2	0.04(s)	-	-	-
Dry additives				
Carbonate	5.0	10.0	18.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	1.0	1.0	1.0	0.5
Lipase	0.4	-	-	0.4
Amylase	0.1	-	-	0.1
Cellulase	0.1	0.2	0.2	0.1
NOBS	-	4.0	-	4.5
PB1	1.0	5.0	1.5	6.0
Sulfate	4.0	5.0	-	5.0
SRPI	-	0.4	-	-

	A	B	C	D
ARP1	0.05	0.08	0.1(es)	-
ARP2	0.05	-	-	0.02(es)
Sud supressor	-	0.5	0.5	-
Misc/minor to 100%				

Example 7

The following granular detergent compositions were prepared in accord with the invention.

	A	B	C
Blown powder			
Zeolite A	20.0	-	15.0
STPP	-	20.0	-
Sulphate	-	-	5.0
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DTPMP	0.4	0.4	0.1
STS	-	-	1.0
Spray on			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
ARP1	0.1(s)	0.05(s)	0.08(s)
Dry additives			
QEA	-	-	1.0
Carbonate	14.0	9.0	10.0
PB1	1.5	2.0	-
PB4	18.5	13.0	13.0

	A	B	C
TAED	2.0	2.0	2.0
QAS (I)	-	-	1.0
Photoactivated bleach	15 ppm	15 ppm	15ppm
SKS-6	-	-	3.0
Protease	1.0	1.0	0.2
Lipase	0.2	0.2	0.2
Amylase	0.4	0.4	0.2
Cellulase	0.1	0.1	0.2
Sulfate	10.0	20.0	5.0
Misc/minors to 100%			
Density (g/litre)	700	700	700

Example 8

The following detergent compositions, according to the present invention were prepared:

	A	B	C
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
EDDS	-	0.4	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			

	A	B	C
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
ARP2	0.02(s)	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
PEO	-	-	0.2
ARP1	0.1	0.2	0.08(ec)
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	850	850	850

	D	E	F	G	H
Blown Powder					
STPP/ Zeolite A	9.0	15.0	15.0	9.0	9.0
Flocculating agent II or III	0.5	0.2	0.9	1.5	-
LAS	7.5	23.0	3.0	7.5	7.5
QAS	2.5	1.5	-	-	-
DTPMP	0.4	0.2	0.4	0.4	0.4
HEDP or EDDS	-	0.4	0.2	-	-

CMC	0.1	0.4	0.4	0.1	0.1
Sodium carbonate	5.0	20.0	20.0	10.0	-
Brightener	0.05	-	-	0.05	0.05
Clay I or II	-	10.0	-	-	-
STS	0.5	-	-	0.5	0.5
MA/AA	1.5	2.0	2.0	1.5	1.5
Agglomerates					
Suds suppresser (silicon)	1.0	1.0	-	2.0	0.5
Agglomerate					
Clay	9.0	-	-	4.0	10.0
Wax	0.5	-	-	0.5	1.5
Glycerol	0.5	-	-	0.5	0.5
Agglomerate					
LAS	-	5.0	5.0	-	-
TAS	-	2.0	1.0	-	-
Silicate	-	3.0	4.0	-	-
Zeolite A	-	8.0	8.0	-	-
Carbonate	-	8.0	4.0	-	-
Spray On					
Perfume	0.3	-	-	0.3	0.3
C45E7 or E9	2.0	-	-	2.0	2.0
C25E3 or E4	2.0	-	-	2.0	2.0
Dry additives					
Citrate or citric acid	2.5	-	2.0	2.5	2.5
Clay I or II	-	5.0	5.0	-	-
Flocculating agent I or II	-	-	-	-	0.2
Bicarbonate	-	3.0	-	-	-
Carbonate	15.0	-	-	25.0	31.0
TAED	1.0	2.0	5.0	1.0	-
Sodium perborat or percarbonate	6.0	7.0	10.0	6.0	-
SRP1, 2, 3 or 4	0.2	0.1	0.2	0.5	0.3

CMC or nonionic cellulose ether	1.0	1.5	0.5	-	-
Protease	0.3	1.0	1.0	0.3	0.3
Lipase	-	0.4	0.4	-	-
Amylase	0.2	0.6	0.6	0.2	0.2
Cellulase	0.2	0.6	0.6	0.2	0.2
Silicone antifoam	-	5.0	5.0	-	-
Perfume (starch)	0.2	0.3	1.0	0.2	0.2
Speckle	0.5	0.5	0.1	-	1.0
NaSKS-6 (silicate 2R)	3.5	-	-	-	3.5
Photobleach	0.1	-	-	0.1	0.1
Soap	0.5	2.5	-	0.5	0.5
Sodium sulfate	-	3.0	-	-	-
ARP1	0.1	1.0(d)	0.05	3.0(es)	0.09
Misc/minors to 100%	100.0	100.0	100.0	100.0	100.0
Density (g/litre)	850	850	850	850	850

Example 9

The following detergent formulations, according to the present invention were prepared:

	A	B	C	D
LAS	18.0	14.0	24.0	20.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C23E56.5	-	-	1.0	-
C45E7	-	1.0	-	-
C45E3S	1.0	2.5	1.0	-
STPP	32.0	18.0	30.0	22.0
Silicate	9.0	5.0	9.0	8.0
Carbonate	11.0	7.5	10.0	5.0
Bicarbonate	-	7.5	-	-

	A	B	C	D
PB1	3.0	1.0	-	-
PB4	-	1.0	-	-
NOBS	2.0	1.0	-	-
DTPMP	-	1.0	-	-
DTPA	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1
MA/AA	1.0	1.5	2.0	0.5
CMC	0.8	0.4	0.4	0.2
PEI	-	-	0.4	-
Sodium sulfate	20.0	10.0	20.0	30.0
Mg sulfate	0.2	-	0.4	0.9
Protease	0.8	1.0	0.5	0.5
Amylase	0.5	0.4	-	0.25
Lipase	0.2	-	0.1	-
Cellulase	0.15	-	-	0.05
Photoactivated bleach (ppm)	30ppm	20ppm	-	10ppm
ARP3	0.04(s)	0.08(ec)	0.1(s)	0.04(es)
Perfume spray on	0.3	0.3	0.1	0.2
Brightener 1/2	0.05	0.2	0.08	0.1
Misc/minors to 100%				

Example 10

The following liquid detergent formulations were prepared in accord with the invention (levels are given as parts per weight).

	A	B	C	D	E
LAS	11.5	8.8	-	3.9	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	15.7	-
C23E9	-	2.7	1.8	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.2	-	3.1
TPKFA	1.6	-	2.0	0.5	2.0
Citric acid (50%)	6.5	1.2	2.5	4.4	2.5
Calcium formate	0.1	0.06	0.1	-	-
Sodium formate	0.5	0.06	0.1	0.05	0.05
Sodium cumene sulfonate	4.0	1.0	3.0	1.18	-
Borate	0.6	-	3.0	2.0	2.9
Sodium hydroxide	5.8	2.0	3.5	3.7	2.7
Ethanol	1.75	1.0	3.6	4.2	2.9
1, 2 propanediol	3.3	2.0	8.0	7.9	5.3
Monoethanolamine	3.0	1.5	1.3	2.5	0.8
TEPAE	1.6	-	1.3	1.2	1.2
Protease	1.0	0.3	1.0	0.5	0.7
Lipase	-	-	0.1	-	-
Cellulase	-	-	0.1	0.2	0.05
Amylase	-	-	-	0.1	-
SRP1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
ARP1	0.3	-	-	0.1	-
ARP2	-	0.04	-	-	0.1
ARP3	-	-	0.3	-	-
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Water/minors					

Exempl 11

The following liquid detergent formulations were prepared in accord with the invention (levels are given in parts per weight):

	A	B	C	D	E	F	G	H
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
APA	-	1.4	-	-	3.0	1.0	2.0	-
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0
Citric acid	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Rape seed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	-	-
TEPAE	0.5	-	0.5	0.2	-	-	0.4	0.3
DTPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
Protease	0.5	0.5	0.4	0.25	-	0.5	0.3	0.6
Alcalase	-	-	-	-	1.5	-	-	-
Lipase	-	0.10	-	0.01	-	-	0.15	0.15
Amylase	0.25	0.25	0.6	0.5	0.25	0.9	0.6	0.6
Cellulase	-	-	-	0.05	-	-	0.15	0.15
Endolase	-	-	-	0.10	-	-	0.07	-
SRP2	0.3	-	0.3	0.1	-	-	0.2	0.1
Boric acid	0.1	0.2	1.0	2.0	1.0	1.5	2.5	2.5
Calcium chloride	-	0.02	-	0.01	-	-	-	-
Bentonite clay	-	-	-	-	4.0	4.0	-	-
Brightener 1	-	0.4	-	-	0.1	0.2	0.3	-

	A	B	C	D	E	F	G	H
Sud supressor	0.1	0.3	-	0.1	0.4	-	-	-
Opacifier	0.5	0.4	-	0.3	0.8	0.7	-	-
ARP1	0.3	-	0.1	-	0.05	-	0.1	0.08
ARP2	-	0.04	-	0.02	-	0.1	0.08	0.1
Water/minors								
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2

Example 12

The following liquid detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	A	B
LAS	27.6	18.9
C45AS	13.8	5.9
C13E8	3.0	3.1
Oleic acid	3.4	2.5
Citric acid	5.4	5.4
Sodium hydroxide	0.4	3.6
Calcium formate	0.2	0.1
Sodium formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	5.9	5.5
Xylene sulfonic acid	-	2.4
TEPAE	1.5	0.8
Protease	1.5	0.6
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume spray on	0.5	0.3
ARP1	0.3	-
ARP3	-	0.04
Water/minors		

Exempl 13

The following is a composition in the form of a tablet, bar, extrudate or granule in accord with the invention

	A	B	C	D	E	F	G
Sodium C ₁₁ -C ₁₃ alkylbenzenesulfonate	12.0	16.0	23.0	19.0	18.0	20.0	16.0
Sodium C ₁₄ -C ₁₅ alcohol sulfate		4.5	-		-	-	4.0
C ₁₄ -C ₁₅ alcohol ethoxylate (3) sulfate	-	-	2.0	-	1.0	1.0	1.0
Sodium C ₁₄ -C ₁₅ alcohol ethoxylate	2.0	2.0	-	1.3	-	-	5.0
C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt			-	-	1.0	0.5	2.0
Tallow fatty acid			-	-	-	-	1.0
Sodium tripolyphosphate / Zeolite	23.0	25.0	14.0	22.0	20.0	10.0	20.0
Sodium carbonate	25.0	22.0	35.0	20.0	28.0	41.0	30.0
Sodium Polyacrylate (45%)	0.5	0.5	0.5	0.5	-	-	-
Sodium polyacrylate/maleate polymer	-	-	1.0	1.0	1.0	2.0	0.5
Sodium silicate (1:6 ratio NaO/SiO ₂)(46%)	3.0	6.0	9.0	8.0	9.0	6.0	8.0
Sodium sulfate	-	-	-	-	-	2.0	3.0
Sodium perborate/percarbonate	5.0	5.0	10.0	-	3.0	1.0	-
Poly(ethyleneglycol), MW ~4000 (50%)	1.5	1.5	1.0	1.0	-	-	0.5
Sodium carboxy methyl cellulose	1.0	1.0	1.0	-	0.5	0.5	0.5
NOBS/ DOBS	-	1.0	-	-	1.0	0.7	-

TAED	1.5	1.0	2.5	-	3.0	0.7	-
SRP 1	1.5	1.5	1.0	1.0	-	1.0	-
Clay I or II	5.0	6.0	12.0	7.0	10.0	4.0	3.0
Flocculating agent I or III	0.2	0.2	3.0	2.0	0.1	1.0	0.5
Humectant	0.5	1.0	0.5	1.0	0.5	0.5	-
Wax	0.5	0.5	1.0	-	-	0.5	0.5
Moisture	7.5	7.5	6.0	7.0	5.0	3.0	5.0
Magnesium sulphate	-	-	-	-	-	0.5	1.5
Chelant	-	-	-	-	0.8	0.6	1.0
Enzymes, including amylase, cellulase, protease and lipase	-	-	-	-	2.0	1.5	2.0
ARP2	0.3	3.0(d)	-	-	-	-	-
ARP1	0.08	0.1	3.0(d)	1.5(es)	0.05	1.0(d)	0.05
Speckle	2.5	4.1	4.2	4.4	5.6	5.0	5.2
minors, e.g. perfume, PVP, PVPVI/PVNO, brightener, photo-bleach,	2.0	1.0	1.0	1.0	2.5	1.5	1.0

	H	I	J	K
Sodium C ₁₁ -C ₁₃ alkylbenzenesulfonate	23.0	13.0	20.0	18.0
Sodium C ₁₄ -C ₁₅ alcohol sulfate	-	4.0	-	-
Clay I or II	5.0	10.0	14.0	6.0
Flocculating agent I or II	0.2	0.3	0.1	0.9
Wax	0.5	0.5	1.0	-
Humectant (glycerol/ silica)	0.5	2.0	1.5	-
C ₂ -C ₁₅ alcohol ethoxylate sulfate	-	-	-	2.0
Sodium C ₁₄ -C ₁₅ alcohol ethoxylate (2.5	3.5	-	-
C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt	-	-	-	0.5
Tallow fatty acid	0.5	-	-	-
Tallow alcohol ethoxylate (50)	-	-	-	1.3
Sodium tripolyphosphate	-	41.0	-	20.0
Zeolite A, hydrate (0.1-10 micron size)	26.3	-	21.3	-

Sodium carbonate	24.0	22.0	35.0	27.0
Sodium Polyacrylate (45%)	2.4	-	2.7	-
Sodium polyacrylate/maleate polymer	-	-	1.0	2.5
Sodium silicate (1.6 or 2 or 2.2 ratio NaO/SiO ₂)(46%)	4.0	7.0	2.0	6.0
Sodium sulfate	-	6.0	2.0	-
Sodium perborate/ percarbonate	8.0	4.0	-	12.0
Poly(ethyleneglycol), MW ~4000 (50%)	1.7	0.4	1.0	-
Sodium carboxy methyl cellulose	1.0	-	-	0.3
Citric acid	-	-	3.0	-
NOBS/ DOBS	1.2	-	-	1.0
TAED	0.6	1.5	-	3.0
Perfume	0.5	1.0	0.3	0.4
SRP 1	-	1.5	1.0	1.0
Moisture	7.5	3.1	6.1	7.3
Magnesium sulphate	-	-	-	1.0
Chelant	-	-	-	0.5
speckle	1.0	0.5	0.2	2.7
Enzymes, including amylase, cellulase, protease and lipase	-	1.0	-	1.5
ARP1	0.1	3.0(d)	1.0(es)	0.3
minors. e.g. brightener, photo-bleach	1.0	1.0	1.0	1.0

Example 14

The following laundry bar detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	A	B	C	D	E	F	G	H
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Sodium laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Calcium carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0

	A	B	C	D	E	F	G	H
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DTPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Protease	-	0.12	-	0.08	0.08	-	-	0.1
Lipase	-	0.1	-	0.1	-	-	-	-
Amylase	-	-	0.8	-	-	-	0.1	-
Cellulase	-	0.15	-	-	0.15	0.1	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
ARP1	0.3	-	-	0.04	-	0.5	-	-
ARP2	-	0.04	-	-	0.1	-	0.08	-
ARP3	-	-	0.3	-	-	-	-	0.3
Brightener	0.15	0.10	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

Example 15

The following detergent additive compositions were prepared according to the present invention :

	A	B	C
LAS	-	5.0	5.0
STPP	30.0	-	20.0
Zeolite A	-	35.0	20.0
PB1	20.0	15.0	-

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	A	B	C
TAED	10.0	8.0	-
ARP1	0.3	-	0.1
ARP2	-	0.04	0.02
Protease	-	0.3	0.3
Amylase	-	0.06	0.06
Minors, water and miscellaneous	Up to 100%		

Example 16

The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared according to the present invention :

	A	B	C	D	E	F	G	H
STPP	-	-	54.3	51.4	51.4	-	-	50.9
Citrate	35.0	17.0	-	-	-	46.1	40.2	-
Carbonate	-	17.5	14.0	14.0	14.0	-	8.0	32.1
Bicarbonate	-	-	-	-	-	25.4	-	-
Silicate	32.0	14.8	14.8	10.0	10.0	1.0	25.0	3.1
Metasilicate	-	2.5	-	9.0	9.0	-	-	-
PB1	1.9	9.7	7.8	7.8	7.8	-	-	-
PB4	8.6	-	-	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.7	11.8	4.8
Nonionic	1.5	2.0	1.5	1.7	1.5	2.6	1.9	5.3
TAED	5.2	2.4	-	-	-	2.2	-	1.4
HEDP	-	1.0	-	-	-	-	-	-
DTPMP	-	0.6	-	-	-	-	-	-
MnTACN	-	-	-	-	-	-	0.008	-
PAAC	-	-	0.008	0.01	0.007	-	-	-
BzP	-	-	-	-	1.4	-	-	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.6	-	-
ARP3	0.1	0.3	0.2	0.05	-	-	-	0.8
ARP1	-	-	-	-	0.3	0.03	0.5	-
Protease	0.072	0.072	0.029	0.053	0.046	0.026	0.059	0.06
Amylase	0.012	0.012	0.006	0.012	0.013	0.009	0.017	0.03
Lipase	-	0.001	-	0.005	-	-	-	-
BTA	0.3	0.3	0.3	0.3	0.3	-	0.3	0.3

[illegible]

Example 17

The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention :

[illegible]

Exempl 18

The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm² using a standard 12 head rotary press:

	A	B	C	D	E	F
STPP	-	48.8	49.2	38.0	-	46.8
Citrate	26.4	-	-	-	31.1	-
Carbonate	-	5.0	14.0	15.4	14.4	23.0
Silicate	26.4	14.8	15.0	12.6	17.7	2.4
ARP1	0.3	-	-	-	0.06	-
ARP2	-	0.04	-	-	-	0.08
ARP3	-	-	0.3	0.1(ec)	-	-
Protease	0.058	0.072	0.041	0.033	0.052	0.013
Amylase	0.01	0.03	0.012	0.007	0.016	0.002
Lipase	0.005	-	-	-	-	-
PB1	1.6	7.7	12.2	10.6	15.7	-
PB4	6.9	-	-	-	-	14.4
Nonionic	1.5	2.0	1.5	1.65	0.8	6.3
PAAC	-	-	0.02	0.009	-	-
MnTACN	-	-	-	-	0.007	-
TAED	4.3	2.5	-	-	1.3	1.8
HEDP	0.7	-	-	0.7	-	0.4
DTPMP	0.65	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.55	-	-
BTA	0.2	0.3	0.3	0.3	-	-
PA30	3.2	-	-	-	-	-
MA/AA	-	-	-	-	4.5	0.55
Perfume	-	-	0.05	0.05	0.2	0.2
Sulphate	24.0	13.0	2.3	-	10.7	3.4
Weight of tablet	25g	25g	20g	30g	18g	20g
pH	10.6	10.6	10.7	10.7	10.9	11.2
Miscellaneous and water	Up to 100%					

Example 19

The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared according to the present invention :

	A	B	C	D
STPP	17.5	17.5	17.2	16.0
Carbonate	2.0	-	2.4	-
Silicate	5.3	6.1	14.6	15.7
NaOCl	1.15	1.15	1.15	1.25
Polygen/carbopol	1.1	1.0	1.1	1.25
Nonionic	-	-	0.1	-
NaBz	0.75	0.75	-	-
ARP3	0.3	0.5	0.05	0.1
NaOH	-	1.9	-	3.5
KOH	2.8	3.5	3.0	-
pH	11.0	11.7	10.9	11.0
Sulphate, miscellaneous and water	up to 100%			

Example 20

The following liquid rinse aid compositions were prepared according to the present invention :

	A	B	C
Nonionic	12.0	-	14.5
Nonionic blend	-	64.0	-
Citric	3.2	-	6.5
HEDP	0.5	-	-
PEG	-	5.0	-
SCS	4.8	-	7.0
Ethanol	6.0	8.0	-
ARP1	0.3	-	0.1
ARP2	-	0.04	0.01
pH of the liquid	2.0	7.5	/
Miscellaneous and water	Up to 100%		

Exempl 21

The following liquid dishwashing compositions were prepared according to the present invention :

	A	B	C	D	E
C17ES	28.5	27.4	19.2	34.1	34.1
Amine oxide	2.6	5.0	2.0	3.0	3.0
C12 glucose amide	-	-	6.0	-	-
Betaine	0.9	-	-	2.0	2.0
Xylene sulfonate	2.0	4.0	-	2.0	-
Neodol C11E9	-	-	5.0	-	-
Polyhydroxy fatty acid amide	-	-	-	6.5	6.5
Sodium diethylene penta acetate (40%)	-	-	0.03	-	-
TAED	-	-	-	0.06	0.06
Sucrose	-	-	-	1.5	1.5
Ethanol	4.0	5.5	5.5	9.1	9.1
Alkyl diphenyl oxide disulfonate	-	-	-	-	2.3
Ca formate	-	-	-	0.5	1.1
Ammonium citrate	0.06	0.1	-	-	-
Na chloride	-	1.0	-	-	-
Mg chloride	3.3	-	0.7	-	-
Ca chloride	-	-	0.4	-	-
Na sulfate	-	-	0.06	-	-
Mg sulfate	0.08	-	-	-	-
Mg hydroxide	-	-	-	2.2	2.2
Na hydroxide	-	-	-	1.1	1.1
Hydrogen peroxide	200ppm	0.16	0.006	-	-
ARP3	0.3	-	0.1	-	0.1
ARP1	-	0.3	-	0.1	0.1
Protease	0.017	0.005	0.0035	0.003	0.002
Perfume	0.18	0.09	0.09	0.2	0.2
Water and minors	Up to 100%				

Exempl 22

The following liquid hard surface cleaning compositions were prepared according to the present invention :

	A	B	C	D	E
ARP2	0.04	-	0.08	-	0.01
ARP3	-	0.3	-	0.125	0.1
Amylase	0.01	0.002	0.005	-	-
Protease	0.05	0.01	0.02	-	-
Hydrogen peroxide	-	-	-	6.0	6.8
Acetyl triethyl citrate	-	-	-	2.5	-
DTPA	-	-	-	0.2	-
Butyl hydroxy toluene	-	-	-	0.05	-
EDTA*	0.05	0.05	0.05	-	-
Citric / Citrate	2.9	2.9	2.9	1.0	-
LAS	0.5	0.5	0.5	-	-
C12 AS	0.5	0.5	0.5	-	-
C10AS	-	-	-	-	1.7
C12(E)S	0.5	0.5	0.5	-	-
C12,13 E6.5 nonionic	7.0	7.0	7.0	-	-
Neodol 23-6.5	-	-	-	12.0	-
Dobanol 23-3	-	-	-	-	1.5
Dobanol 91-10	-	-	-	-	1.6
C25AE1.8S	-	-	-	6.0	-
Na paraffin sulphonate	-	-	-	6.0	-
Perfume	1.0	1.0	1.0	0.5	0.2
Propanediol	-	-	-	1.5	-
Ethoxylated tetraethylene pentaamine	-	-	-	1.0	-
2, Butyl octanol	-	-	-	-	0.5
Hexyl carbitol**	1.0	1.0	1.0	-	-
SCS	1.3	1.3	1.3	-	-
pH adjusted to	7-12	7-12	7-12	4	-
Miscellaneous and water	Up to 100%				

*Na₄ ethylenediamine diacetic acid

**Diethylene glycol monohexyl eth r

Example 23

The following spray composition for cleaning of hard surfaces and removing household mildew was prepared according to the present invention :

ARP2	0.04
Amylase	0.01
Protease	0.01
Na octyl sulfate	2.0
Na dodecyl sulfate	4.0
Na hydroxide	0.8
Silicate	0.04
Butyl carbitol*	4.0
Perfume	0.35
Water/minors	up to 100%

*Diethylene glycol monobutyl ether

Example 24

The following lavatory cleansing block compositions were prepared according to the present invention.

	A	B	C
C16-18 fatty alcohol/50EO	80.0	-	-
LAS	-	-	80.0
Nonionic	-	1.0	-
Oleoamide surfactant	-	26.0	-
Partially esterified copolymer of vinylmethyl ether and maleic anhydride, viscosity 0.1-0.5	5.0	-	-
Polyethylene glycol MW 8000	-	39.0	-
Water-soluble K-polyacrylate MW 4000-8000	-	12.0	-
Water-soluble Na-copolymer of acrylamide (70%) and acrylic acid (30%) low MW	-	19.0	-
Na triphosphate	10.0	-	-
Carbonate	-	-	8.0
ARP2	0.04	-	0.01
ARP3	-	0.25	0.1